

Figure 3

(top) Soil samples were taken at several depths from a contaminated site. (bottom) Model compounds derived from polarized-EXAFS data at the ESRF and μ -EXAFS data at the ALS provide a good fit with powder-EXAFS spectra from a soil sample, thereby confirming the identification of the contaminating species.

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Publication

1. A. Manceau et al, "Quantitative Zn speciation in smelter-contaminated soils by EXAFS spectroscopy," *Am. J. Sci.* (in press, 2000).

Microbial Reduction of Hexavalent Chromium

Compounds containing chromium atoms are potentially hazardous contaminants in the environment. The degree of hazard depends on the chemical state of the chromium in the compounds in which it occurs. Chromium with a positive charge of +6 is highly soluble in water and therefore mobile in the environment, so the contamination spreads, and it is toxic and carcinogenic. However, chromium with a positive charge of +3 is relatively insoluble in water and significantly less harmful. Processes that convert chromium from the +6 to the +3 state are potentially useful for waste cleanup and environmental remediation. Berkeley Lab researchers working at the ALS have used an infrared microscope to demonstrate that certain bacteria found naturally in rocks are effective agents in the "biogeochemical" transformation of chromium from the undesirable +6 state to the less harmful +3 state, thereby resolving an on-going controversy about the nature of the conversion.

Hexavalent chromium (Cr^{6+}) is a widespread contaminant that enters the environment through various industrial processes. Cr^{6+} compounds are highly water soluble, toxic in the environment, and carcinogenic in mammals. However, recent studies have shown that certain bacterial species in geologic materials can detoxify the compounds by reducing them to relatively insoluble and hence significantly less harmful trivalent chromium (Cr^{3+}) compounds, a process known as biogeochemical transformation. We have used the Fourier-transform infrared (FTIR) spectromicroscopy beamline (Beamline 1.4.3) to obtain spatially resolved, time-dependent spectra that give evidence of the biogeochemical transformation of Cr^{6+} .

This is the first time that biogeochemical transformation of Cr^{6+} by microorganisms on a mineral surface has been nondestructively monitored and studied. Because infrared light does not kill bacteria, the transformation of Cr^{6+} can be monitored where it occurs. Distinct and relevant infrared absorption bands related to the transformation are used not

only as chemical markers to detect different chromium species, but also as biological markers to detect the presence and activity of microorganisms on specimen surfaces. In addition, the brightness of the infrared radiation from the beamline makes spatially resolved spectroscopy (spectromicroscopy) possible.

Two reduction mechanisms had previously been postulated for the reduction of Cr^{6+} compounds. The biological mechanism requires the presence of microorganisms to aerobically reduce the Cr^{6+} . The chemical mechanism relies on metal oxides, such as Fe(II) compounds, to catalyze the Cr^{6+} -reduction reaction. We conducted FTIR experiments to distinguish the relative significance of these two mechanisms. In addition, we evaluated the effects of common organic co-contaminants, such as toluene vapor, on the biotic reduction process.

For magnetite surfaces of mixed iron oxides that contain no living microorganisms, a five-day exposure to Cr^{6+} compounds resulted in no statistically significant changes in infrared chemical markers, indicating that no catalysis of Cr^{6+} reduction was occurring. On samples with living microorganisms, however, some Cr^{6+} reduction was detected. Moreover, when the samples with living microorganisms were incubated in dilute toluene vapor, statistically significant changes in both infrared-absorption

intensity and characteristic band shapes were observed for Cr^{6+} , as were new bands signaling the possible existence of intermediate Cr^{5+} . FTIR spectromicroscopy showed that the changes in the infrared absorption bands occurred at the sites of bacterial concentration. Imaging the surface at characteristic absorption bands showed a strong correlation between peak depletion of Cr^{6+} and toluene and peak concentration of biological molecules.

In a study to determine if this microbial reduction process could occur in real geologic samples, composite mineral surfaces of basalt rock chips containing resident communities of microbes were exposed to solutions of Cr^{6+} and toluene vapor. At the end of four months, FTIR spectromicroscopy showed that Cr^{6+} -tolerant and Cr^{6+} -reducing natural microorganisms were thriving in association with Cr^{3+} (Figure 4). The reduced Cr^{3+} state was confirmed by x-ray absorption fine structure (XAFS) spectroscopy at Beamline 10.3.2.

The nondestructive infrared spectromicroscopy studies, combined with XAFS spectroscopy and microbiological techniques, show that highly mobile and toxic Cr^{6+} contaminants can be biologically reduced into less soluble, less toxic Cr^{3+} compounds. The FTIR method can now be expanded to examine other infrared-amenable microbial/chemical contaminant systems.

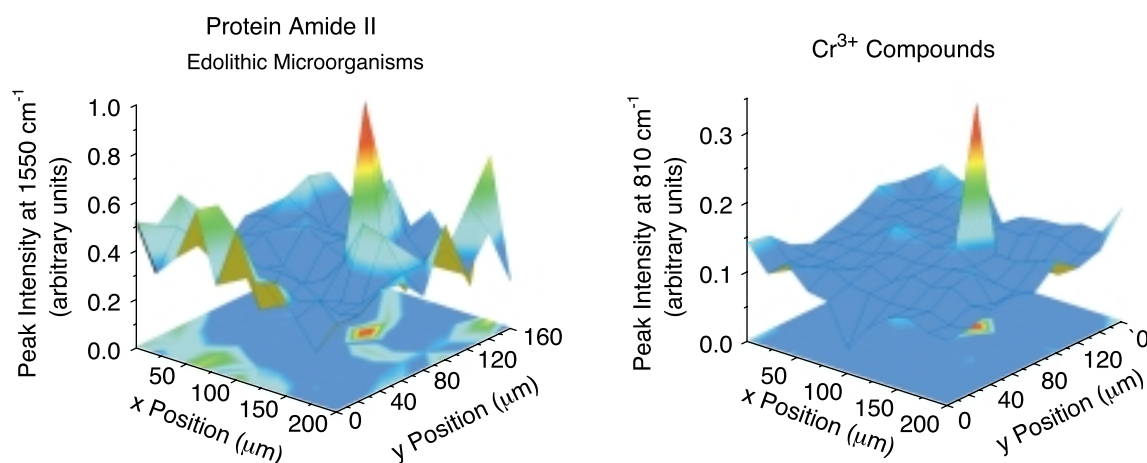


Figure 4

After a four-month exposure of basalt rock chips to solutions of Cr^{6+} and toluene vapor, SR-FTIR spectromicroscopy showed that Cr^{6+} -tolerant and Cr^{6+} -reducing natural microorganisms (left) were thriving in association with Cr^{3+} (right).

Investigators

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Publication

1. H.-Y. N. Holman et al., “Real-time characterization of biogeochemical reduction of Cr(VI) on basalt surfaces by SR-FTIR imaging,” *Geomicrobiology J.* **16**, 307(1999).